[DESCRIPTION]

[Invention Title]

POROUS COATED MEMBER AND MANUFACTURING METHOD THEREOF USING COLD SPRAY

[Technical Field]

The present invention relates, in general, to a coated member on which a porous coating layer is formed and a method of producing the same and, more particularly, to a method of forming a porous coating layer on a surface of mother material using a low temperature spraying process and a coated member in which a pore distribution and a size of the coating layer are controlled.

[Background Art]

Formed on a surface of a member, a porous coating layer improves thermal and mechanical properties of the member.

For example, if a porous coating layer which includes open pores communicating with each other is formed on the surface of a heat exchanger, the heat exchanger has an increased area of contact with surrounding air, thereby assuring efficient heat exchanging performance. Meanwhile, sometimes, it is expected for a friction member to have low strength and hardness depending on its relationship with

surrounding components. The porous coating layer can satisfy this requirement. Furthermore, when mother material is joined with a different kind of material, stress may occur due to lattice misalignment at an interface. The porous coating layer can act as a buffer layer for avoiding stress during the joining.

Conventionally, various coating methods have been employed as a method of forming a metal coating layer on the surface of a member for thermal and mechanical applications. With respect to this, the method may be exemplified by an electro-plating process, a hot dip plating process, or thermal spraying process. However, these processes have limits in terms of application, or may cause thermal impact to the mother material or thermal deformation of the mother material. Additionally, in practice, it is difficult to artificially control the porosity and pore distribution of the coating layer using the above processes.

As well, the thermal conductive metal coating layer which is applied to pipes of the conventional heat exchanger corrodes or is mossy on a surface thereof in a corrosive environment, such as waste water or sea water, thus it does not perform its function. Accordingly, it is problematic in that durability is not assured.

【Detailed description of Invention】

An object of the present invention is to provide a member for thermal and mechanical applications, which does not cause thermal deformation of mother material or damage to the mother material due to thermal impact and which is capable of being applied to various fields, and a method of forming a porous coating layer used in the member.

Another object of the present invention is to provide a member for thermal and mechanical applications, in which porosity, a pore size, and a pore distribution of a surface coating layer are capable of being controlled, a method of forming a porous coating layer used in the member, and a porous coated member produced using the method.

A further object of the present invention is to provide a method of forming a porous coating layer having high thermal conductivity, which is capable of being used in an external corrosive environment for a long time.

In order to accomplish the above objects, the present invention provides a method of forming a porous coating layer on mother material. The method comprises providing the mother material, feeding powder having a metal composition, which includes at least two different metals selected from the group consisting of Al, Mg, Zn, and Sn and which is expressed by $xA-(1-x)B$ ($0<x<1$, x is a weight ratio of A and B), onto the mother material, supplying high pressure gas to the powder, applying the metal powder on the mother material by spraying the metal powder using the

high pressure gas through an supersonic nozzle, and heat-treating the coated mother material to form the porous coating layer.

According to an embodiment of the present invention, in the method as described above, A is Al, and B includes a metal element selected from the group consisting of Mg, Zn, and Sn. Furthermore, it is preferable that the heat-treatment of the coated mother material be conducted at a temperature between a eutectic temperature of A and B and a melting point of a metal having the higher melting point of A and B. In detail, the heat-treatment is conducted at about 200 - 650℃.

Additionally, the feeding of the powder may further comprise changing x to change the composition of the powder.

As well, the present invention provides a metal coated member. The metal coated member comprises metal mother material, and a coating layer formed on the metal mother material, which includes at least two metal elements and is expressed by xA-(1-x)B (x is a weight ratio of A and B). A and B are different metals selected from the group consisting of Al, Mg, Zn, and Sn, x changes when moving in a thickness direction of the coating layer within a range of $0< x <1$, and porosity of the coating layer is changed depending on a change in x.

According to the embodiment of the present invention,

in the above member, x increases or decreases moving in a thickness direction of the coating layer, and the porosity of the coating layer is increased or decreased as x is increased or decreased. Additionally, A is Al, B is any one metal selected from the group consisting of Mg, Zn, and Sn, and x is decreased and the porosity of the coating layer is increased moving from an interface of the metal mother material and the coating layer to a surface of the coating layer.

As well, the present invention provides a metal coated member. The metal coated member comprises metal mother material, and a coating layer formed on the metal mother material, which includes at least two metal elements and is expressed by A-B. A and B are different metals selected from the group consisting of Al, Mg, Zn, and Sn, A or B selected from the above group changes when moving in a thickness direction of the coating layer, and porosity of the coating layer is changed depending on a change in A or B.

In the present invention, the coating layer may include open pores which are at least partially interconnected with each other, and it is preferable that the open pores exist in an upper part of the coating layer in specific application fields.

Additionally, the present invention provides a method of forming a porous carbon coating layer on mother

material. The method comprises providing the mother material, feeding carbon powder which is conglomerated by an organic binder, supplying high pressure gas to the carbon powder, and applying the carbon powder on the mother material by spraying the carbon powder using the high pressure gas through a supersonic nozzle.

In the above method, the organic binder which is used to make the carbon powder coarse may be at least one selected from the group consisting of polyvinyl alcohol (PVA), rosin, resin, polyvinyl butyral (PVB), and polyethylene glycol (PEG). It is preferable that the organic binder be contained in a content of 10 - 30 wt% based on carbon.

Furthermore, in the above method, the coating layer may be additionally subjected to a step of burning out the organic binder at 400 - 500℃.

【Brief Description of Drawings】

FIG. 1 schematically illustrates a low temperature spraying system 100 used to form a coating layer in the present invention;

FIGS. 2a and 2b are flow charts showing the formation of the porous coating layer, according to an embodiment of the present invention;

FIG. 3 is a sectional view of a coated member 200 which includes a coating layer having a variable

composition, according to the embodiment of the present invention;

FIG. 4 is an optical microscope picture of a section of a coating layer having a composition of 0.5Al-0.5AlMg after heat treatment, according to the embodiment of the present invention;

FIG. 5 is an optical microscope picture of a section of a coating layer having a composition of 0.3Al-0.7AlMg after heat treatment, according to the embodiment of the present invention;

FIG. 6 is an optical microscope picture of a section of a coating layer in which Al/AlMg/Al/AlMg/Al components are sequentially layered after heat treatment, according to the embodiment of the present invention;

FIG. 7 is an optical microscope picture of a section of a coating layer in which 0.667Al-0.333Mg/0.5Al-0.5Mg components are sequentially layered after heat treatment, according to the embodiment of the present invention;

FIG. 8 is an optical microscope picture of a section of a coating layer having a composition of 0.5Al-0.5Sn after heat treatment, according to the embodiment of the present invention;

FIG. 9 is an optical microscope picture of a section of a coating layer in which 0.667Al-0.333Sn/0.5Al-0.5Sn components are sequentially layered after heat treatment, according to the embodiment of the present invention;

FIG. 10 is an optical microscope picture of a section of a coating layer in which 0.667Al-0.333Zn/0.5Al-0.5Zn components are sequentially layered after heat treatment, according to the embodiment of the present invention;

FIG. 11 is a flow chart showing the formation of a porous carbon coating layer, according to another embodiment of the present invention; and

FIGS. 12a and 12b are electron microscope pictures of a section and a surface of the carbon coating layer formed through the procedure of FIG. 11.

【Best Mode】

Hereinafter, a detailed description will be given of the present invention, referring to the drawings.

FIG. 1 schematically illustrates a low temperature spraying device 100 which accelerates powder to form a coating layer on a substrate (S) in the present invention.

The spraying device 100 accelerates the powder for forming the coating layer at subsonic or supersonic speed to apply it to the substrate (S). With respect to this, the spraying device 100 comprises a gas compressor 110, a gas heater 120, a powder feeder 130, and a spraying nozzle 140.

The powder of about 1 - 50 μm fed from the powder feeder 130 is sprayed using compressed gas of about 5 - 20 atm supplied from the gas compressor 110 through the spraying nozzle 140 at a rate of about 300 - 1200 mm/s. The

powder sprayed in conjunction with the gas collides with the substrate (S). In this regard, kinetic energy of the powder plastically deforms the powder when the powder collides against the substrate (S), and provides bonding strength to the substrate, thereby forming the coating layer having very high density.

In the device 100, the gas heater 120 which is positioned in a path for feeding the compressed gas is a supplementary unit for heating the compressed gas to increase the kinetic energy of the compressed gas so as to increase the spraying speed of the spraying nozzle. Furthermore, as shown in the drawing, a portion of the compressed gas may be fed from the gas compressor 110 into the powder feeder 130 so as to nicely feed the powder into the spraying nozzle 140.

The compressed gas for the device 100 may be exemplified by some commercial gases, such as helium, nitrogen, argon, or air, and the kind of gas used may be appropriately selected in consideration of the spraying speed of the spraying nozzle 140 and economic efficiency.

The operation and structure of the device are disclosed in detail in US. Pat. No. 5,305,414 by Anatoly P. Alkimov *et al.*, and a description of them is omitted herein.

FIG. 2a is a flow chart showing the formation of the coating layer on the mother material or the substrate using

the spraying device described referring to FIG. 1.

With reference to FIG. 2a, the method of the present invention starts from the step (S210) of feeding metal powder containing two or more metals from the powder feeder 130 of the spraying device 100 and the step (S220) of feeding compressed gas at high pressure from the gas compressor 110.

In the step (S210) of feeding the powder, the powder containing two or more metals includes a mixture or a solid solution of at least two metals selected from the group consisting of Al, Mg, Zn, and Sn, or a mixture of both. Furthermore, the metals selected in the present invention are different from each other. For example, if one metal selected from the above group includes Al, a composition of the metal powder may be a binary system, such as Al-Mg, Al-Zn, or Al-Sn, a ternary system, such as Al-Mg-Zn, or a system having more than three metals. Additionally, in addition to the enumerated metals, Ti, Si, Mn, Cr, Fe, Co, Ni, or Cu may be also used without departing from the spirit of the present invention.

In the present invention, the powder having the metal components may be provided in the form of solid solution. For example, the metal powder containing Al-Mg may be provided in the form of AlMg solid solution which is so-called Magal. In addition, the powder having the metal components may be provided in a mixture of the solid

solution powder and the monolith powder. For example, the metal powder may be a mixture of Al powder and AlMg powder. Since the metal powder containing Mg is dangerous to handle, for example, it may cause explosions, it is provided as a solid solution to assure ease of handling.

When the coating layer of the present invention is used in members having thermal and mechanical applications, since the metal powder has relatively good thermal and mechanical properties, such as thermal conductivity or strength, compared to its specific gravity, it is preferable that it contain Al or an Al alloy extensively used in machine members.

In the step (S220) of feeding the compressed gas of the present invention, the gas may be exemplified by helium, nitrogen, argon, or air as described above. The gas is compressed by the gas compressor to pressure of about 5 - 20 atm and is then provided. If necessary, the compressed gas may be provided while being heated to about 200 - 500℃ using a heating unit, such as the gas heater 120 of FIG. 1. However, even though the compressed gas is heated according to the embodiment, the temperature change of the metal powder is insignificant due to the very low specific gravity of the gas. Accordingly, the spraying step of the present invention is different from a conventional spraying process, in which the powder is heated and coated at a melting point or higher, in that the spraying is conducted

at low temperatures.

Meanwhile, as described above, a portion of the compressed gas used in the step (S220) of feeding the compressed gas may be used as carrier gas for continuously and stably feeding the metal powder.

Next, a mixture of the compressed gas and the metal powder is sprayed using the supersonic spraying nozzle (S230). The flow rate of the gas-powder mixture sprayed through the nozzle depends on the temperature and pressure of the gas and the particle size and specific gravity of the powder. The gas-powder mixture having the particle size of about 1 - 50 ㎛ is sprayed at the rate of about 300 - 1200 m/s under the pressure and temperature conditions of the fed gas.

The metal powder which is sprayed at the high rate collides against the mother material to form the high density coating layer. The spraying step (S230) is conducted until the coating layer having a desired thickness is formed, and the coating layer thus formed is then heat treated (S240). In the present invention, it is preferable that the heat treatment temperature be about 200 - 650℃. The heat treatment temperature of 650℃ or higher causes complete melting of the metal coat, and the coat is barely melted at the temperature of 200℃ or lower, resulting in a negligible heat treatment effect.

The high density coating layer formed on the mother

material is subjected to the heat treatment step (S240) to acquire porosity. As well, as seen in the embodiment described later, porosity and the pore size of the porous coating layer depend on the change in composition of the applied metal powder. In this regard, the "change in composition" as used herein is intended to include a change in quantity as well as metals used.

FIG. 2b shows the method of forming the porous coating layer, which comprises the step (S250) of changing the composition of the metal powder so as to control a pore distribution of the coating layer, with respect to the coating method of the present invention described referring to FIG. 2a.

According to the method, the composition of the powder is changed in the course of forming the coating layer during the step of spraying using the nozzle (S240). For example, after the powder having the composition of 0.5Al-0.5Mg, in which a weight ratio of Al:Mg is 1:1, is fed for a predetermined time, the ratio is controlled to 1:2, or the powder having Al-Zn instead of Al-Mg, in which a ratio of Al:Zn is 1:1, is fed, thereby forming the coating layer which has a vertical composition gradient or contains different components.

The change in composition of the powder may be achieved through a typical procedure well known to those skilled in the art. For example, powders having different

compositions may be sequentially fed into one powder feeder, or, after a plurality of powder feeders for storing the powders having the different compositions are prepared, the powder feeder containing the powder having the desired composition may be selected using valves.

FIG. 3 is a sectional view of a coated member 200 which includes the coating layer formed through the procedure.

With reference to FIG. 3, an Al-Zn layer 210 having a weight ratio of 2:1, an Al-Zn layer 220 having a weight ratio of 1:1, and an Al-Zn layer 230 having a weight ratio of 1:2 are formed on the mother material (S), such as Al. According to the embodiment of the present invention as described later, if the coating layer is heat treated, the Zn content increases, thus increasing the pore size and porosity. Hence, if the member which is coated with the powder having the composition shown in FIG. 3 is heat treated, it is possible to form the coated member in which porosity and/or a pore volume increase moving away from the mother material. The pore distribution as described above is desirable because it contributes to the stable coating at an interface between the coating layer and the mother material. Furthermore, in the structure as describe above, since porosity and the pore volume increase, the pores formed at an outermost surface of the coating layer may be open pores communicating with each other. Particularly, the

open pores play an important role in improving a heat exchanging property of the mother material.

As described above, the change in pore distribution of the coating layer, which is described referring to FIG. 3, may be obtained by changing the quantities of the components or by changing the types of components. In other words, it is possible to produce a coated member, in which porosity and/or the pore size increase moving away from the interface, by sequentially layering Al-Mg, Al-Zn, and Al-Sn layers on the mother material.

FIG. 11 is a flow chart showing the formation of a porous carbon coating layer, according to another embodiment of the present invention.

With reference to FIG. 11, first, carbon powder having an average particle size of 10 ㎛ or less is mixed with at least one binder selected from the group consisting of PVA, PVB, PEG, resin, and rosin (S310). The mixing is conducted using a suitable solvent, that is, an organic solvent, such as water or alcohol, depending on the type of binder.

Subsequently, the resultant slurry is dried to produce a carbon powder cake, and the cake is pulverized and sorted, thereby producing carbon powder having a particle size that is suitable to the nozzle spraying, for example, an average particle size of 50 - 200 ㎛ (S320 to S340). Thereafter, the carbon powder is conglomerated using

the organic binder to be made coarse in comparison with the original size of the powder.

Next, the resulting carbon powder is sprayed in conjunction with high pressure gas of about 4 - 7 kgf/cm^2 (S350) using a low temperature spraying device described referring to FIG. 1 through the nozzle so as to form the coating layer on the mother material (S350). In addition, a burn out process may be conducted at about 400 - 500℃ to remove the organic binder from the coating layer.

A better understanding of the present invention may be obtained through the following preferred examples.

Physical properties of metals used in the following examples 1 to 7 are described in Table 1.

TABLE 1

Metal	Melting point(℃)	Density(g/cm^2)
Al	660.2	2.699
Mg	650	1.74
Zn	419.46	7.133
Sn	231.9	7.298

Spraying conditions of a nozzle in examples 1 to 7 are as follows.

- Nozzle : standard laval type
  aperture : 4 X 6 mm
  throat gap : 1 mm
- Compressed gas : type : air
  pressure : 7 atm
  temperature : 330℃

- Size of powder fed : < 44 μm (325 mesh)

EXAMPLE 1

Mixture powder which includes Al powder and AlMg powder (eutectic temperature of about 400℃) in a weight ratio of 50:50 (i.e. 0.5Al-0.5AlMg) and air at 7 atm were fed into a spraying nozzle to be applied on an aluminum substrate.

The resulting coating was heat treated at about 620℃ for 1 hour. The heat treated substrate was cut and polished, and cross section was observed using an optical microscope. FIG. 4 illustrates a picture of the cut surface of the resultant substrate.

From FIG. 4, it can be seen that the coating layer is nicely attached to the Al substrate. An interface between the Al substrate and the coating layer is apparent due to pores (black portions) trapped in the coating layer. The pores were not observed during the coating, but were generated after the heat treatment.

EXAMPLE 2

A coating layer was produced under the same conditions as example 1 except that the weight of AlMg increased in the mixture powder so that the metal powder

had a composition of 0.3Al-0.7AlMg. The coating layer was heat treated, a section was observed using an optical microscope, and the results are shown in FIG. 5.

In comparison with FIG. 4, from FIG. 5, it can be seen that the size of the pore is increased, and an increase in porosity can be confirmed even with the naked eye.

EXAMPLE 3

A coating layer was formed in such a way that Al powder/AlMg powder/Al powder/AlMg powder/Al powder were sequentially layered. The remaining coating conditions were the same as example 1. Subsequently, the resulting coating layer was heat treated at 620℃ for 1 hour.

FIG. 6 is an optical microscope picture showing a section of a heat treated substrate. As shown in the drawing, pores were scarcely observed in the Al layer, but frequently observed in the AlMg layer.

EXAMPLE 4

An Al substrate was coated with mixture powder having a composition of 0.667Al-0.333Mg, and then with another mixture powder having a composition of 0.5Al-0.5Mg. The remaining coating conditions were the same as example 1.

Subsequently, the resulting coating layer was heat treated at about 620℃ for 1 hour, and a section was observed using an optical microscope.

FIG. 7 is an optical microscope picture of the section. From FIG. 7, it can be seen that the porosity of a coating portion (an outermost surface) having the composition of 0.5Al-0.5Mg is higher than that of a coating portion (an interface) having the composition of 0.667Al-0.333Mg. Accordingly, it can be seen that the porosity of the coating layer increases as the Mg content increases. Additionally, from the shape of the pores and the porosity, it may be presumed that the pores at the outermost surface are open pores communicating with each other. As described above, the pores, which are interconnected with each other and are distributed from the outermost surface of the coating layer to the inside thereof, increase the area of contact with surrounding air. Thus, particularly, it is available to applications requiring excellent heat exchanging or heat radiation properties.

EXAMPLE 5

An Al substrate was coated with mixture powder of Al and Sn, which had a composition of 0.5Al-0.5Sn. The remaining coating conditions were the same as in example 1.

The resulting coating layer was heat treated at about

650℃ for 1 hour, and a section was observed using an optical microscope after it was polished. FIG. 8 is an optical microscope picture of the section. As shown in FIG. 7, very many pores were observed in the coating layer. Judging from the shape of the pores and the porosity, the pores seem to be interconnected with each other.

EXAMPLE 6

Mixture powder having a composition of 0.667Al-0.333Sn was applied through the same procedure as in example 1, and another mixture powder having a composition of 0.5Al-0.5Sn was subsequently applied. The resulting coating layer was heat treated at 620℃ for 1 hour, and a polished section was observed using an optical microscope.

FIG. 9 is a picture of the section. From comparison of an interface portion coated with 0.667Al-0.333Sn with an outermost surface portion coated with 0.5Al-0.5Sn, it can be seen that the pore size is significantly higher and porosity is higher at the outermost surface portion. Accordingly, it can be seen that an increase in the Sn content promotes the generation of pores.

EXAMPLE 7

An Al substrate was coated with mixture powder having

a composition of 0.667Al-0.333Zn, and then with another mixture powder having a composition of 0.5Al-0.5Zn. The coating conditions were the same as example 1. Subsequently, the resulting coating layer was heat treated at about 620℃ for 1 hour, a section was observed using an optical microscope, and the results are shown in FIG. 10.

From FIG. 10, it can be seen that many pores are formed in the coating layer due to the addition of Zn. Additionally, it can be seen that very large pores exist and porosity is higher at an outermost surface portion having a high Zn content in comparison with an interface portion having a relatively low Zn content. Therefore, it can be seen that the pore size and porosity increase as the Zn content increases.

From examples 1 to 7, it can be seen that Mg, Zn, and Sn which are added to the coating layer in conjunction with Al contribute to the formation of pores in the coating layer after heat treatment. As well, the pore size and porosity increase as the added amount increases. The pores are interconnected with each other and thus become open pores when the content of Mg, Zn, and Sn increases.

The inventors of the present invention presume that the reason for this is as follows. However, the following description is referentially provided for purposes of understanding of the present invention but is not intended to be a basis for limitation of the scope of the present

invention.

Mg, Zn, and Sn which are added with Al form a eutectic liquid phase in conjunction with Al at a heat treatment temperature, and Al is partially melted. When the liquid phase exists as described above, combination of the pores is relatively easily achieved, thus increasing the pores observed with the naked eye.

Meanwhile, byproduct gases, such as hydrogen, generated through the reaction of molten Al with moisture in the air may be considered the reason for the formation of the pores. It is believed that Mg, Sn, and Zn, which have a melting point lower than Al, as well as Al, cause the above reaction at the heat treatment temperature.

With respect to another reason, it may be presumed that the pores are formed due to a change in density when alloys of metal powders are made through partial melting thereof.

The presumption coincides with the fact that relatively many pores are formed by the addition of Zn or Sn in comparison with the addition of Mg as described in the above examples. The reason is that a melting temperature (419.46℃) of Zn or a melting temperature (231.9℃) of Sn is lower than a melting temperature (650℃) of Mg.

Taking the above into consideration, in the present invention, the heat treatment temperature must be at least

higher than the eutectic temperature of two metals to be mixed with each other. The term "eutectic temperature" as used herein is intended to include a peritectic temperature. However, since the metal powder may contain a small amount of impurities, partial melting may occur at the eutectic temperature or less. Furthermore, in the present invention, the heat treatment temperature must not be higher than the melting point of pure Al, which has the highest melting point. The reason is that the coating will lose structural stability in this case.

EXAMPLE 8

A carbon coating layer was formed on a copper (Cu) plate. After carbon powder having an average particle size of 5 - 10 μm was mixed with about 15 wt% PVA and dried to produce a carbon cake, it was pulverized in a mortar and carbon particles having a particle size of 150 μm or less were sorted. The sorted carbon powder was sprayed onto the copper plate at the same temperature and pressure as in the above examples, thereby forming a carbon coating layer.

FIGS. 12a and 12b are electron microscope pictures of a section and a surface of the carbon coating layer formed on the copper plate. From the drawings, it can be seen that the porous carbon coating layer having excellent adhesion strength was formed on the copper plate.

[Industrial Applicability]

A method of the present invention has the existing advantages of a low temperature spraying process. In other words, since high temperature treatment is not conducted, oxidation of mother material or of a coating layer is maximally suppressed, and damage to the mother material due to heat impact does not occur. Furthermore, a very high coating speed can be assured and it is very easy to control the thickness of the coating layer.

Particularly, Mg, Sn, and Zn, which are used in conjunction with Al in the coating method of the present invention, have a melting point lower than Al. Accordingly, since heat treatment is conducted at a melting point of Al or less, the present invention can be applied to most members for thermal and mechanical applications, which include Al or an Al alloy as a mother material, without damage to the mother material.

Furthermore, in the coating method of the present invention, the coating composition is changed to change the porosity of the coating layer. Hence, it is possible to very easily form porous coating layers needed in various industrial fields through the above method.

As well, in a coated member produced according to the method of the present invention, it is possible to freely control pore size and porosity. Therefore, it can be used

in various members for thermal and mechanical applications.

Additionally, in a carbon coating layer produced according to the method of the present invention, high thermal conductivity is assured due to a porous structure having many pores, and carbon is much more stable in a corrosive environment, such as sea water or waste water, than metal, thus it is suitable to be used as a member for thermal applications in corrosive environments.